

**Title:** The Forcing of Mercury Oxidation as a Means of Promoting Capture  
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Grant No.: DE-FG26-01NT41288  
Period of performance: September 24, 2001 through September 23, 2002

### Abstract

Mercury that exits the furnace in the oxidized form ( $\text{HgCl}_2$ ), as opposed to elemental mercury, is known to be much more easily captured in existing pollution control equipment (*e.g.*, wet scrubbers for  $\text{SO}_2$ ). This is principally due to its high solubility in water. Field data indicate a considerable scatter in the oxidized versus elemental split for mercury. Until recently, however, nobody knew what caused this oxidation, why there is so much scatter, or how to promote the oxidation as a means of favoring capture.

Recent DOE-funded research in our group that is continued by the present grant, along with work by others, has identified the gas phase mechanism responsible for this oxidation. The scenario is as follows. In the flame the mercury is quantitatively vaporized as elemental mercury. Also, the chlorine in the fuel is released as HCl. The direct reaction  $\text{Hg} + \text{HCl}$  is well known to be far too slow to be of practical consequence in oxidation. The high temperature region does, however, generate a small concentration of atomic chlorine from the HCl. As the gases cool (either in the furnace convective passes, or within a sample probe), the decay in Cl atom is constrained by the slowness of the principal recombination reaction,  $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$ . This allows chlorine atom to hold a temporary, local superequilibrium concentration. Once the gases drop below about  $550^\circ\text{C}$ , the mercury equilibrium shifts to favor  $\text{HgCl}_2$  over Hg, and this superequilibrium chlorine atom promotes oxidation via the fast reactions  $\text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$ ,  $\text{HgCl} + \text{Cl} + \text{M} \rightarrow \text{HgCl}_2 + \text{M}$ , and  $\text{HgCl} + \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Cl}$ . Thus, the high temperature region provides the Cl needed for the reaction, while the quench region allows the Cl to persist and oxidize the mercury in the absence of decomposition reactions that would destroy the  $\text{HgCl}_2$ .

This mechanism is successful in explaining why many of the earlier laboratory studies of mercury oxidation showed more oxidation at high temperatures than low temperatures, in contradiction with equilibrium. In each case, the high temperature experiments were followed by a thermal quench to room temperature before the mercury measurements were performed. The high temperatures are needed to generate chlorine atom, but no significant oxidized mercury is present at high temperatures due to the

presence of fast  $\text{HgCl}_2$  destruction reactions. Instead, the oxidized mercury is formed during the thermal quench. The apparent correlation between furnace temperature and oxidation occurs because the higher temperatures result in higher chlorine atom concentrations, resulting in more oxidation during quench.

Another feature that was difficult to explain was the significant difference in the amount of oxidation observed between experiments that used similar reaction times and temperatures. In particular, those experiments that did not include water vapor in the reaction mixture showed much more oxidation than the corresponding wet experiments. Under the present grant we systematically examined the influence of water vapor concentration and found it does have a significant influence on oxidation. Chemical kinetic modeling suggests that the presence of water significantly reduces the concentrations of chlorine atom present in the high temperature region. This results in less oxidation during the quench.

Our present experiments focus on the use of trace amounts of  $\text{H}_2$  as a promoter for mercury oxidation. The idea is that chain branching during  $\text{H}_2$  reaction will promote the conversion of  $\text{HCl}$  to  $\text{Cl}$ . The chemical kinetics suggest that this is a complex process, and that the temperature at the addition point and the amount of  $\text{H}_2$  used are critical. For example, addition of  $\text{H}_2$  at too high a temperature appears to actually decrease  $\text{Cl}$  concentrations via  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ . At lower temperatures this reaction is slowed due to its activation energy. Thus, within the correct window, the process is predicted to become selective for  $\text{Cl}$  promotion. Preliminary data suggest that this is the case. Only relatively small amounts of  $\text{H}_2$  are indicated as being needed, and these could be provided by a small natural gas reformer on site.

Our next task focuses on the use of trace  $\text{O}_2$  as an additive under rich conditions, targeting mercury oxidation within coal syngas streams. The oxidized mercury would then be removed during the cold gas cleanup steps.